ELECTROLYTIC DEPOSITION OF COPPER FROM MATTE

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ARMOUR INSTITUTE OF TECHNOLOGY

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Electrolytic deposition of copper from matte

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ELECTROLYTIC DEPOSITION OF COPPER
FROM MATTE.

A THESIS

Presented by

W. H. Wiard

H. C. Smith

to the

President and Faculty

of

Armour Institute of Technology

for the Degree of

Bachelor of Science in Chemical Engineering,

Having Completed the Prescribed Course of

Study in

Chemical Engineering

1909.

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-: Preface :-

Part I.

The object of this part is to determine the most efficient working temperature, and current density, and all other experimental data connected with the process.

Part II.

This chapter deals with a description of of the proposed plant, giving an idea of the process, the cost of operation, and the anticipated profits.

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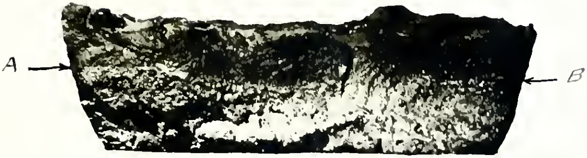
Part I.

The object of this part is to determine the most efficient working temperature, and current density, and all other experimental data connected with the process.

Electrolytic Deposition of Copper from Matte.

The object of this work is to secure an economical method for the separation of copper from a matte which is obtained by the Great Western Smelting Company. This company is located at West Kinzie and Halsted Streets and melts junk containing lead, copper, zinc, tin, etc and either separates these metals or obtains an alloy of them. When the metal has been heated until in a molten condition it is poured into moulds and this matte rises to the top of the mould and when cooled is taken to a small reverberatory furnace. The lead is here sweated out until as much is removed as can be economically done.

The experimental work was carried on with this matte to find the best conditions for the electrolytic refining of the copper present. The different factors which influenced the rate of deposit and cost are strength of electrolyte, temperature of the electrolyte, current density, and voltage; and the work will be divided under these headings.



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Preparation of the Metal.

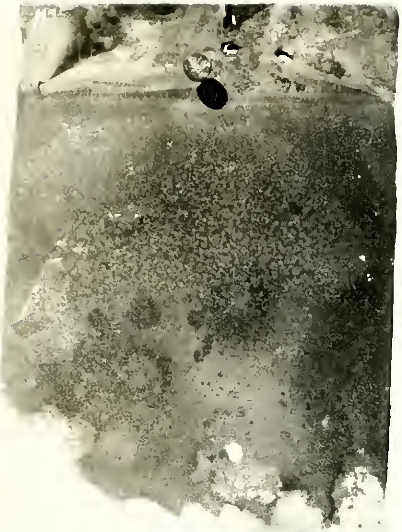
The accompanying photograph shows a cross-sectional view of the matte as it is obtained after the lead has been sweated out. The line AB shows distinctly the division of the rich matte from the matte that contains very little copper and is mostly lead. The matte was prepared for experimental work by melting in a crucible in a muffle furnace and casting into thin moulds averaging about 1/4" to 3/8" in thickness. The photograph which is full size, shows a type of the plates that were used in all the experimental work. Before any electrolytic work was done an analysis of the matte after casting into plates was made and gave the following analysis;

Cu - 49.39%
Pb - 19.10%
Zn - 3.80%
Sn - 15.20%
Sb - 1.50%

Determination of the Most Efficient Temperature and Current Density.

This work was carried on with two pure copper plates as cathodes and a plate of the matte as the anode. The strengths of the electrolyte used were one of 16% $CuSO_4 \cdot 5H_2O$ and 9% H_2SO_4, this being the strength of the commercial solution used in multiple system refineries and the other solution consisted of 16% $CuSO_4 \cdot 5H_2O$ and 6% H_2SO_4, this being the strength of the commercial solution used in series refineries. Rectangular glass jars were used, having a capacity of about 350 cc. Very little work was done using the latter solution as it was found that the solution of 9% H_2SO_4 gave the best results in the amount of copper deposited in a unit of time.

Before starting each run the cathodes were carefully cleansed by dipping in a solution of nitric acid after which they were washed in distilled water, rinsed with alcohol and dried over a Bunsen flame. After this preparation they were carefully weighed and the anode or matte plate was also weighed.



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The most efficient temperature and current density were determined by a series of runs starting with a temperature of 40°C and increasing in increments of 10° until a temperature of 80°C was reached.

The current density used varied from one ampere per square decimeter by increments of one half ampere until a current density of four amperes per square decimeter was reached.

The accompanying photograph shows to some extent the effect of temperature on the evenness of deposition of the copper. These plates show the deposit for 50°, 60°, 70°, and 80°C with a current density of 3½ amperes per square decimeter. Plate 'A' was run at a temperature of 50°C and shows a coherent deposit though it is somewhat rough. Plate 'C' was run at 60°C and shows a fairly good deposition although it is not a smooth deposit. Plate 'B' was run at 70°C and shows a good coherent deposit very fine in grain as is the best of all the runs. Plate 'D' shows the deposit at 80°C which may be seen to be uneven in deposition with the formation of trees.

Calculation of Efficiency of Current.

Theoretically one ampere current deposits .0003294 grams of copper per second. Then the theoretical deposit is equal to .0003294 x 5 x 3600 as the length of the run was five hours. Then the theoretical deposit is equal to 5.929 grams of copper. The actual deposit for this run was 3.4421 grams which gives as efficiency of 58%.

Runs at 40°C.

Amp/sq.dm.	Actual dep.	Theor. dep.	%Eff.
1.0	3.4421	5.9292	58.0
1.5	5.5920	8.8938	64.0
2.0	8.1937	11.8584	69.0
2.5	10.9463	14.8230	74.0
3.0	13.3102	17.7876	75.0
3.5	16.1804	20.7522	78.0
4.0	18.0327	23.7168	76.0

Runs at 50°C.

Amp/sq.dm.	Actual dep.	Theor. dep.	%Eff.
1.0	3.3864	5.9292	57.0
1.5	5.7816	8.8938	65.0
2.0	8.2459	11.8584	69.5
2.5	10.8816	14.8230	73.4
3.0	13.6101	17.7876	76.3
3.5	16.8006	20.7522	81.0
4.0	19.4107	23.7168	81.6

Runs at 60°C.

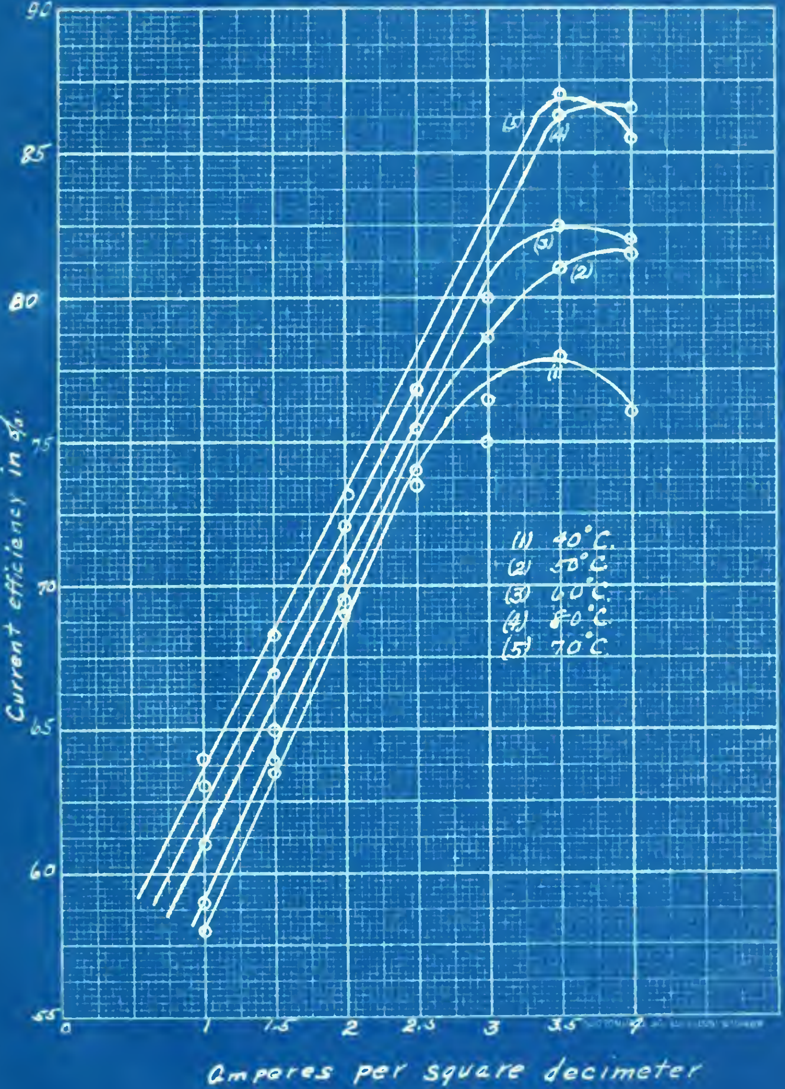
1.0	3.6102	5.9292	61.0
1.5	6.0714	8.8938	67.0
2.0	8.3564	11.8584	70.2
2.5	11.1987	14.8230	75.6
3.0	13.9162	17.7876	78.2
3.5	17.0137	20.7522	82.3
4.0	19.5021	23.7168	81.9

Runs at 70°C.

Amp/sq.dm.	Actual Dep.	Theor.Dep.	%Eff.
1.0	3.7916	5.9292	64.0
1.5	6.0714	8.8938	68.2
2.0	8.6541	11.8584	72.1
2.5	11.3673	14.8230	76.8
3.0	14.1631	17.7876	79.7
3.5	18.0616	20.7522	87.2
4.0	2o.2413	23.7168	85.6

Runs at 80°C.

1.0	3.7437	5.9292	63.0
1.5	6.0020	8.8938	67.4
2.0	8.7101	11.8584	73.2
2.5	11.3106	14.8230	76.4
3.0	14.0879	17.7876	79.1
3.5	18.0372	20.7522	87.0
4.0	20.5310	23.7168	86.2


90
85
80
75
70
65
60
55
Current efficiency in %.
0
1
1.5
2
2.5
3
3.5
4
Amperes per square decimeter
(1)
(2)
(3)
(4)
(5)
(1) 40°C.
(2) 50°C.
(3) 60°C.
(4) 80°C.
(5) 70°C.

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To apply the results to the commercial problem of copper refining, curves were drawn showing the relation between the amperes per square decimeter and the current efficiency for each temperature of the electrolyte. From these curves it may be seen that the current efficiency is highest for an amperage of 3.5 amperes per square decimeter and a temperature of 70°C for the electrolyte. The current efficiency is high as obtained experimentally on a small scale and will undoubtedly be less in real practice, reaching in some cases as low as 65% for these values of current and temperature. This loss of energy is due to bad metal contacts and short-circuiting and partly to the use of voltages much in excess to those actually required to overcome the resistance of the solution.

With a current density of 3.5 amperes per square decimeter no extra power will be required to heat the electrolyte, for when operating at this current density the current alone is sufficient to heat the electrolyte to 70°C.

Determination of the Voltage.

With a constant value of current it may be seen from Ohm's law, R = E/I, that the addition of more resistance will necessitate a higher voltage. Now the operating voltage will depend upon the number of tanks in series and the distance between the electrodes. This value of voltage cannot be definitely determined until commercial conditions are met with but is taken from determinations made in practice by Prof. W. D. Bancroft of Cornell University under similar conditions. This value is taken as fifteen volts and is a conservative value for the voltage in a multiple system of tanks .

In summing up the results obtained from the different runs, that in order to operate a plant most economically we find that copper should be refined electrolytically under the following conditions of 3.5 amperes per square decimeter and 70°C temperature of electrolyte.

Purity of Copper Deposited.

Samples of copper were taken from deposits of several plates and analyses made for the purity of the copper obtained. An analysis was made of the deposit upon each plate for an amperage of 3.5 per square decimeter and gave the following analyses:

40°C - - - - - - % Cu 99.20
50°C - - - - - - % Cu 99.38
60°C - - - - - - % Cu 99.36
70°C - - - - - - % Cu 99.71
80°C - - - - - - % Cu 99.53

Five runs were made with a current density of 3.5 amperes per square decimeter and a temperature of 70°C and the deposit removed from the plates and mixed thoroughly and an analysis made for copper. This analysis gave a purity of 99.68 %Cu.

Analysis and Treatment of Sludge.

The sludge produced in the electrolytic refining of copper settled to the bottom of the glass jar. When the run was completed the electrolyte was drawn off and the remaining sludge washed to remove the $CuSO_4$ present and then dried. The sludge from several runs was taken and ground and mixed thoroughly to be taken for an average analysis. This analysis is as follows;

Pb - 50.12%
Sn - 16.00%
Zn - 21.84%
Cu - 1.31%
Sb - 7.26%

The commercial treatment of this sludge is discussed in another chapter of this work.

Part II.

This chapter deals with a description of the proposed plant, giving an idea of the process, the cost of operation, and the anticipated profits.

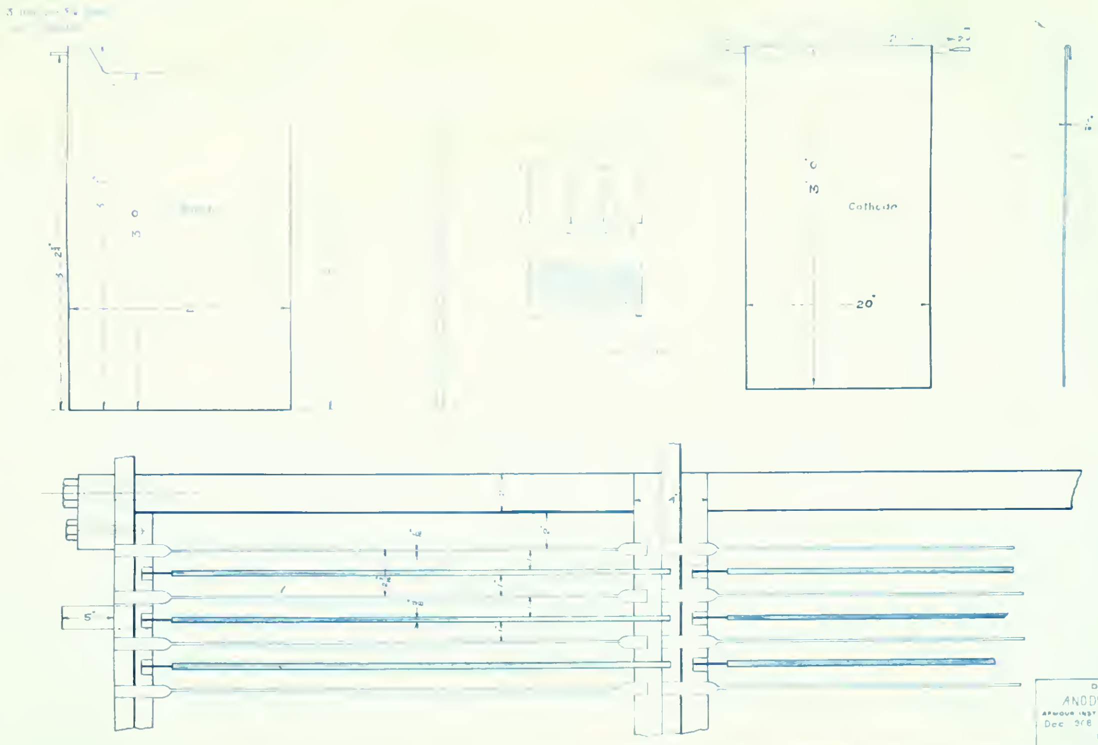
Capitalization.

To treat 10 tons of matte per week will require a plant with a capital investment of about $50,000.00; this will include the entire first costs, as land, construction of buildings, all necessary equipment and a four weeks supply of working material.

The plant is designed to treat the matte for copper by the electrolytic process and the melting of the refined copper and the lead sludge into bar form suitable for the market.

The following is an estimate of the required capital;

Land - - - - - - - - - -	$ 7500.00
Building - - - - - - - -	15000.00
Tanks- - - - - - - - - -	1000.00
Furnaces - - - - - - - -	2000.00
Motor Generator- - - -	1000.00
1 Overhead Crane - - -	750.00
Copper Conductors- - -	800.00
2 Air Compressors- - -	150.00
One Month Stock - - -	2400.00
Material in Process- -	100.00
Cost of Installation -	500.00
Sinking Fund - - - - -	5000.00
Incidentals- - - - - -	13800.00
Total	$ 50000.00



DETAIL .
ANODE and CATHODE
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Anodes and Cathodes.

The design of the anodes and cathodes to be used is shown in drawing No.1. This drawing also shows the method of contact of the electrodes to the copper bars carrying the current.

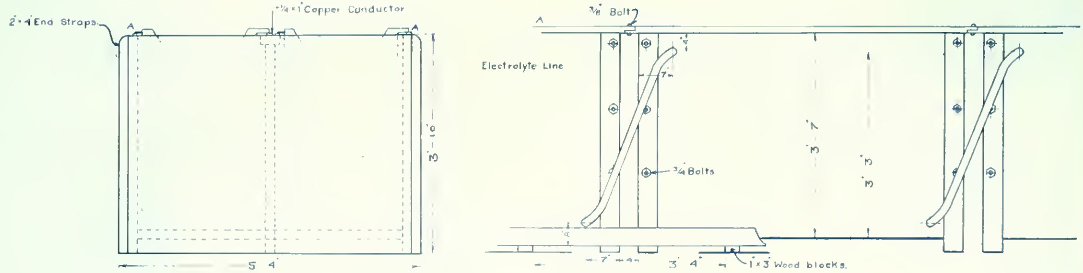
The anodes are made by melting the matte in a reverbatory furnace and pouring into cast iron moulds. The cathodes are made of sheet copper and hang suspended from a twisted copper bar.

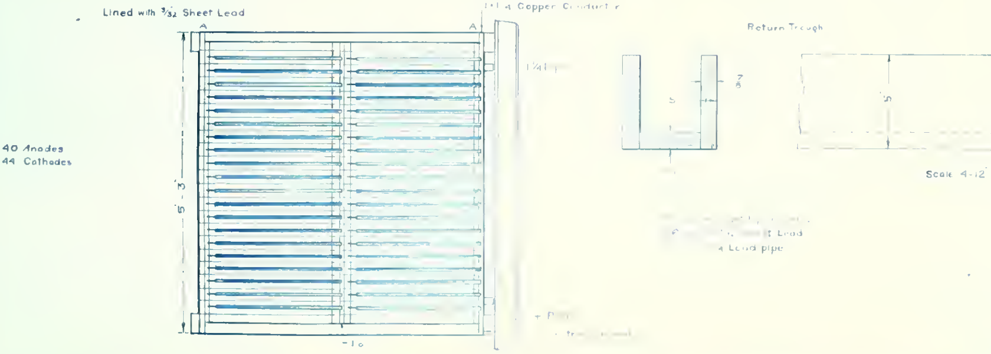
The cathodes before they are ready for service must be cleaned by dipping into a dilute solution of sulphuric acid; when the dirt and the grease have been removed they are passed into a washing tank which contains circulating water; they are now allowed to dry and then coated with paraffin by dipping into a tank of paraffin. This affords a means of stripping the deposited copper from the cathode and saves the expense of making up new ones. All of the above tanks should be located in the furnace room and be of sufficient capacity to treat six cathodes at one operation. All tanks should be constructed of wood and the acid tanks lined with lead.

After the acid sulution has become too weak for further use the dissolved copper from the cathodes may be recovered by adding scrap iron, metallic copper is thrown out of the solution, the supernatant liquid decanted and the copper added to that received from the depositing tanks.

The cathodes are to be transported from the furnace room to the tank room by means of hand cars running on a 20" gauge track. A 15-ton overhead crane operating the entire length of the tank room will pick them up from the car and locate them in their proper position in the tank.

ELECTROLYTIC COPPER REFINING PLANT.





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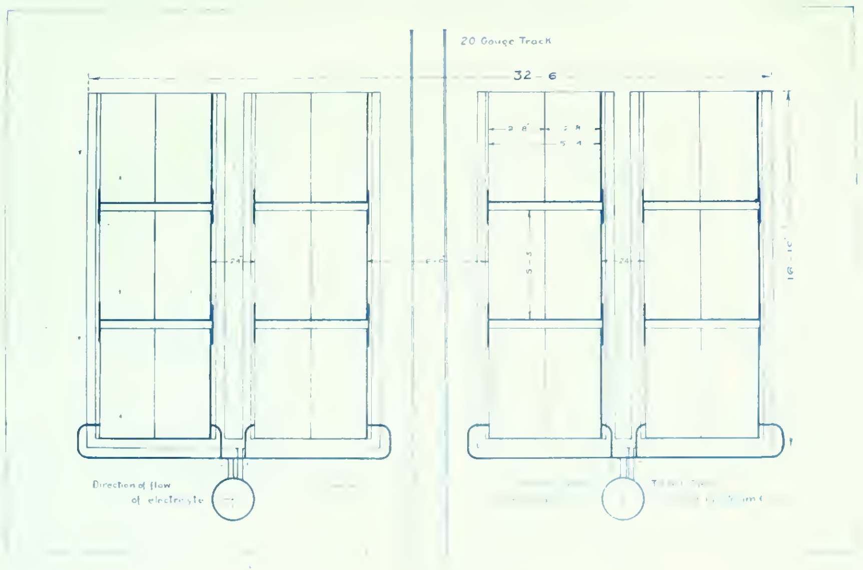
ELECTROLYTIC COPPER REFINING PLANT.



TANK ROOM

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Description of Tanks.

The construction of the tanks and their specifications are shown in drawing No.2. If a current density of 15 amperes per square foot of anode surface is used, the time required for a complete run will be 168 hours or approximately one week. Then it will require 9 tanks in service in order to treat 10 tons of matte per week. Twenty-four tanks should be installed, the extra ones being allowed for use in case of an over-run or while repair work is being done.

The arrangement of the tanks and their piping is shown on drawing No.3. The electrolyte is circulated at the rate of 64 cubic feet per hour by means of a ½ horse-power Westinghouse Air Compressor pump. The electrolyte enters the bottom of the tank at one end and leaves the top at the opposite end thus insuring a steady and complete circulation. The electrolyte after passing through a series of three single tanks returns by gravity to the pump where it is again sent into circulation.

The life of the electrolyte will vary with conditions, depending upon the chemical composition of the matte and the temperature at which the operations are carried on. Probably the electrolyte will be efficient during one complete run, at the end of which it will be discarded. No provisions are made for purifying or refining the electrolyte as the cost would exceed that of making up a fresh solution for a plant of such small capacity.

The following calculations were made in determining the number of tanks required and the length of time for a complete run.

Dimensions of anodes 5/8" x 24" x 36"

Dimensions of cathodes 1/16" x 20" x 36"

Number of anodes to tank - 40

Number of cathodes to tank 42

Electrodes spaced 1" apart.

Assume 95% of the anode surface to be in the electrolyte. Assume specific gravity of matte to be 8.0

Weight of matte per tank

$$= (5/8 \times 24 \times 36)0.95 \times 40 \times \frac{62.5 \times 8}{1728}$$

$$= 5930 \#.$$

Capacity of plant = 10 tons = 20,000#.

No Tanks = $\frac{20000}{5930}$ = 3.46 double tanks.

Anode surface, not including ends,

$= (\frac{24 \times 36}{144})2 \times .95 \times 40 = 556$ sq.ft.

Using 15 amperes per square foot of anode,

556 x 15 = 6840 ampere hours.

1 ampere hour deposits 1.1862 gms copper.

6840 x 1.1862 = 8112 gms copper per hour.

$\frac{8112}{453}$ = 17.90# copper per hour.

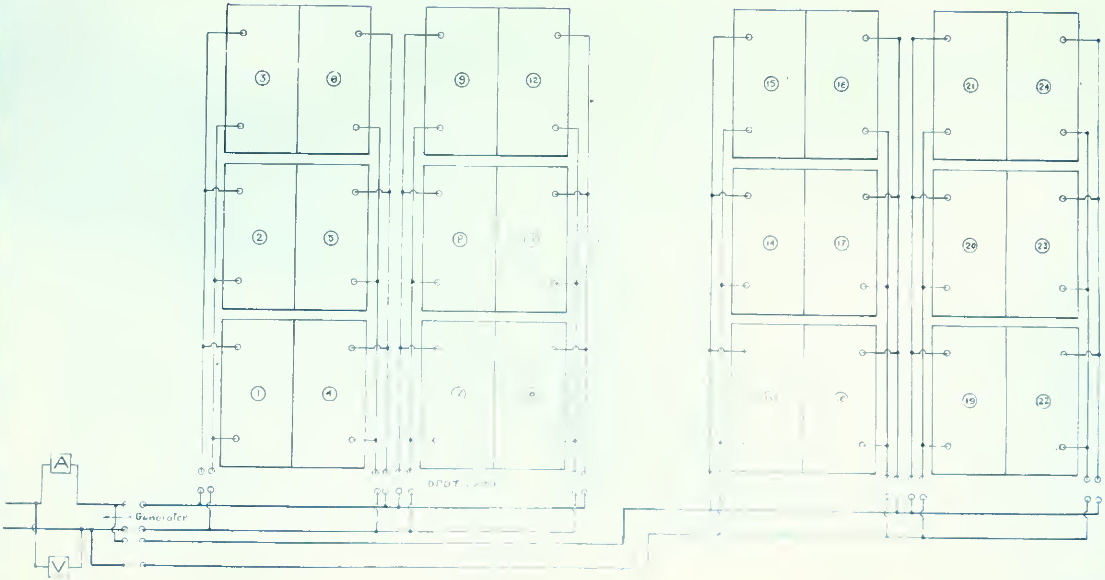
$\frac{5930}{17.9 \times 2}$ = 166 hours per tank for a run.

the above figure is based on the assumption that

the matte is 50% copper

$\frac{166}{24}$ = 6.91 days or one week.

ELECTROLYTIC COPPER REFINING PLANT.



WIRING SYSTEM
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Power.

The required power of 2.5 kilowatts is to be furnished by a Western Electric motor-generator set. The current supplied to the motor is to be bought from the Commonwealth-Edison Company. The motor is driven by alternating current and the generator delivers direct current.

A wiring diagram of the tanks is shown in drawing No.4. The electrodes are connected in multiple and the tanks are connected in series, practice having found this arrangement to be efficient as well as economical. The tanks are wired so that any combination of a series of three single tanks may be thrown into service,.thus the series 1, 2, 3, may be in use or 1, 2, 3,and 18, 20, 21, or any other similiar combination.

Building.

A suitable building for the carrying on of the work of such a plant would require about 8750 square feet of floor space.

The building would be divided at the middle by a brick wall partition, the front part being divided into an office room, laboratory, power room, and tank room. The tank room should have a concrete floor fitted with drains, and should be provided with good light and ventilation. The back part of the building or furnace room will need no floor other than a firm dirt or cinder. The furnace room will contain two reverbatory furnaces, one melting pot, one acid tank, one washing tank, and a paraffin tank.

The two reverbatory furnaces will be constructed of fire brick and designed to satisfy conditions. Each should have a capacity of at least two tons. One furnace is to be used in melting up the matte so that it can be cast into anode plates while the other furnace is to be used in melting up the

stripped copper from the cathodes so that it may be poured into bar form. A two ton melting pot will be sufficient for treating the sludge which is to be poured into bars and sold. The three tanks required in preparing the cathodes should be located near the furnaces to save unnecessary handling of the electrodes. The remaining part of the furnace room is used for storing the raw material and the finished product.

Operating Costs and Anticipated Profits.

The following data on operating costs and anticipated profits is based on one ton of matte, assuming the copper to run 50%, this is probably the maximum percentage, the average being 35%. The annual receipts and expenditures are based upon a working year of fifty weeks.

The market price of electrolytically deposited copper was taken at seventeen cents per pound or $340.00 per ton. The sludge which is of the nature of a hard lead composed of lead sulphate, zinc, tin, and antimony is valued at 4.6 cents per pound or $92.00 per ton. Only 70% of the sludge has been allowed for as being recovered.

The cost of the matte is $.03 per pound or $60.00 per ton.

Calculations for the Costs of Heats:-

The Ostwald calorie is used in all of the following calculations. One Ostwald calorie is equal to 100 small calories.

The following calculations are based upon two tons of matte.

Calories required to melt the copper;

2 tons of matte = 4000#

49.39% Cu present in the matte.

4000 x .4939 = 1975# Cu.

1975 x 453.6 = 895,860 gms Cu.

To melt one gram of copper requires 162 calories,

895,860 x 162 = 145,129,320 calories required to melt the copper in two tons of matte.

Calories required to melt the lead;

19% lead present in the matte.

4000 x .19 = 760# Pb.

760 x 453.6 = 345,040 grams of Pb.

To melt one gram of lead requires 15.6 calories,

345,040 x 15.6 = 5,382,724 calories.

Calories required to melt the tin;

15% Sn present in the matte.

4000 x .15 = 600# Sn.

600 x 453.6 = 272,400 gms Sn.

To melt one gram of tin requires 28?16 calories,

272,400 x 28.16 = 7,670,784 calories.

Calories required to melt zinc;

3.8% Zn present in matte.

4000 x .038 = 152# Zn.

152 x 453.6 = 69,008 gms Zn.

To melt one gram of zinc requires 67.8 calories,

69,008 x 67.8 = 4,678,742 calories.

Total calories required to melt 2 tons matte;

Cu = 145,129,320

Pb = 5,382,624

Sn = 7,670,784

Zn = 4,678,742

Total 162,861,470

Assuming 5% scraps to be remelted,

162,861,470 x .05 = 8,150,000 calories.

Total calories required

= 171,011,000.

Assume coal of 11000B. T. U.

11000 B.T.U. = 6150 calories (small).

$$\frac{171,011,000}{6150 \times 100} = 2760\# \text{ coal required.}$$

Since the furnace efficiency is taken as 50%, to melt one ton of matte will require 2760# coal.

The following are the calculations for finding the calories necessary to melt the sludge.

Calories to melt the lead;

50% Pb present in the sludge.

1000# sludge in 1 ton of matte.

500# lead in 1 ton of matte.

5000 x 453.6 = 227,000 gms Pb.

To melt one gram of lead requires 15.6 calories.

227 x 15.6 = 3,541,2000 calories.

Calories required to melt the tin;

16% Sn present in the sludge.

16% = 160#

160 x 453.6 = 72,640 gms Sn.

To melt one gram of tin requires 28 calories.

72,640 x 28 = 2,033,920 calories.

Calories required to melt the zinc;

25% Zn present in the sludge.

25% = 250#.

250 x 453.6 = 113,500 gms Zn.

To melt one gram of zinc requires 67,8 calories.

113,500 x 67.8 = 7,695,200 calories.

Total heat required to melt the sludge;

Pb = 3,541,000

Sn = 2,033,920

Zn = 7,695,200

Total 13,270,000 calories.

$\frac{13,270,000}{6150 \times 100}$ = 250# coal required.

Calories required to melt the refined Cu.

1000# Cu per ton of matte.

1000 x 453.6 = 453600 gms Cu.

To melt one gram of copper requires 162 calories,

453,600 x 162 = 7,354,800 calories.

$\frac{7,354,800}{6150 \times 100}$ = 120# coal required.

Assume the efficiency of the furnaces as 25%. Then the required amount of coal

= 120 x 4 = 480 or 500#

Grand total of coal;

To melt the matte	2760#
To melt the sludge	500#
To melt the copper	500#
Total	3760#

Assume the price of coal as $2.75 per ton. Then the cost of heats

= $2.75 x 2 = $5.50

Cost of Electrolyte;

The length of a tank is - - - - - 4' 11"

The width of a tank is - - - - - 2' 4"

The depth of electrolyte is - - - 3' 3"

The volume of a double tank

$$= 4.92 \times 2.6 \times 3.25 \times 2 = 82.50 \text{ cu.ft.}$$

The volume of the electrodes

$$= \frac{(5/8 \times 24 \times 36 \times 40) + (1/16 \times 24 \times 36 \times 44)}{1728}$$

$$= 13.70 \text{ cu.ft.}$$

Total electrolyte required

$$= (82.50 - 13.70) \times 3.46 = 238 \text{ cu.ft.}$$

Composition of electrolyte by volume;

$CuSO_4$- - -16% Specific gravity -2.27

H_2SO_4- - - 9% " " 1.84

$238 \times .16 \times 62.5 \times 2.27 = 5387$# $CuSO_4$.

$CuSO_4$ in car load lots at $4.75 per ton

$$\frac{5387 \times 4.75}{2000} = \$10.40 \text{ per run.}$$

$238 \times .09 \times 62.5 \times 1.84 = 2461$# H_2SO_4.

H_2SO_4 in car load lots at $1.75 per ton

$$\frac{2461 \times 1.75}{2000} = \$2.15 \text{ per run.}$$

Cost of electrolyte per ton of matte;

H_2SO_4 - - - - - - \$0.21
$CuSO_4$ - - - - - - \$1.04
Total \$1.25

Cost of circulating electrolyte;

Rate of flow to be 64 cu.ft. per hour.

$\frac{62.5 \times 64}{60} = 66.6$ ft.lbs. per minute.

Estimated cost at 2½ ¢ per hour

$\frac{166 \times 2.5}{10} = \$0.41$ per ton matte.

Cost of power;

Voltage = E = 15 volts.

Amperage = I = 15 amperes per square foot of anode surface.

Anode surface = 2 x 3 x 2 = 12 sq.ft.

$$P = E \times I$$

Power = P = 15 x (15 x 12) = 2.5 kilowatts.

Cost per kilowatt-hour is \$.07.

Cost per ton of matte

$$= \frac{2.5 \times .07 \times 166}{3} = \$10.40$$

Cost of labor;

Estimated at $.75

Salaried help

Estimated at $1.00

Depreciation

$\frac{50000}{500} \times 8\frac{1}{2}\% = \$8.50$ per ton of matte.

Insurance

$\frac{50000}{500} \times 1\% = \$1.00$ per ton of matte.

Taxes

$\frac{50000}{500} \times 1\frac{1}{2}\% = \$1.50$ per ton of matte.

Summary of Costs:-

Matte	$60.00
Coal	5.50
Electrolyte	1.25
Circulation of electrolyte	.41
Power	10.40
Labor	.75
Salaried help	1.00
Depreciation	8.50
Insurance	1.00
Taxes	1.50
Total	$90.31

Valuation of products:-

½ ton of copper	at $340.00 per ton	$170.00
700# sludge	at $ 92.00 " "	32.50
	Total	$202.50

Profit per ton of matte $112.19

Total annual receipts $101,250.00

Total annual expendtiures $ 45,155.00

Per cent profit on capitalization with matte of 50% Cu is 111%.

Per cent profit on capitalization with matte of 35% Cu is 77%.

It is very evident that a bussiness which will pay 77% on its capital is one not to be slighted.

We believe that all of the estimates have been extremely liberal and that if good judgement and supervision were exercised the first costs might be lowered somewhat when the plant is installed. If the plant were operated in connection with other refining processes such as the Great Western Refining Company are carrying on, would also tend to lower the first costs.

With a variation of profit of 77% to 111% and the above considerations taken into account, 100% profit would no doubt be a conservative figure.